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16. ABSTRACT

Methods are described for obtaining ambient PM-10 aerosol data for use in these receptor models. Characteristics of PM-10 sampling devices, filter media and laboratory analysis procedures are described. The latter include x-ray fluorescence, neutron activation, optical spectroscopy, pyrolysis, ion chromatography and colorimetry. It is shown that some combinations of filter medium, sampler and analysis method are incompatible, and information is presented so that incompatibility can be avoided. Measurement artifacts for ionic species and annular denuder systems for avoiding them are described.

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Sampling and Analysis Methods for Ambient PM-10 Aerosol

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1 Introduction

In an early application of receptor models, Friedlander (1973) used data on atmospheric concentrations of Na, Mg, Al, K, Ca, V and Pb to apportion mass concentrations into components related to five different types of emission sources. Improvements in measurement technology enable many more species to be measured, and this can improve the accuracy and resolution of receptor model results. This chapter is intended to provide information for designing a measurement program to obtain ambient aerosol data for use in receptor models. Other chapters in this book show how receptor models are used in air quality management and how species concentrations are used in receptor models.

Primary emphasis in this chapter is given to particles in the PM-10 size range (aerodynamic equivalent diameter less than 10 μm). Characteristics of PM-10 sampling devices and filter media are presented, and the laboratory methods listed in Table 1 are described. It is shown that some combinations of filter medium, air sampler and analysis method are incompatible. Information presented here will enable one to avoid incompatibility and to devise optimum measurement strategies. Measurement artifacts that can alter ionic species concentrations in particles are described, and an annular denuder system for avoiding such artifacts and for measuring gaseous species is described.

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Table 1. Laboratory methods to measure aerosol composition.

Method	Abbrev-iation	Species measured[a]
X-ray fluorescence	XRF	Elements with Z > 12
XRF with energy dispersive detector	EDXRF	Elements with Z > 12
XRF with wavelength dispersive detector	WDXRF	Elements with Z > 12
Particle induced x-ray emission	PIXE	Elements with Z > 12
Instrumental neutron activation analysis	INAA	More than 25 elements
Atomic absorption	AA	One element per lamp
Inductively coupled plasma	ICP	More than 12 elements
Pyrolysis in helium		Volatilizable carbon
Pyrolysis in helium with oxygen		Total carbon
Accelerator mass spectrometry	AMS	^{13}C and ^{14}C
Ion chromatography	IC	Ions in solution
Colorimetry		Ions in solution

[a]The symbol Z represents atomic number.

2 Air sampling

The monitoring requirements for determining attainment of the U. S. Environmental Protection Agency (EPA) National Ambient Air Quality Standard for PM-10 are defined so that sampling devices that meet certain performance specifications can be designated as reference methods (Purdue, 1988). By 1987, PM-10 high volume (hi vol) sampling systems made by Wedding and Associates, Inc. (Fort Collins, CO) and Andersen Samplers, Inc. (Atlanta, GA) had been designated as reference methods (Purdue, 1988). In 1979, the dichotomous sampler made by Andersen Samplers, Inc., was designated as a PM-10 reference method (EPA, 1989). Table 2 shows some of the characteristics of these reference methods and indicates that the devices differ in inlet type and flow rate. A feature unique

to the dichotomous sampler is the use of a virtual impactor to collect particles in fine (0 to 2.5 μm) and coarse (2.5 to 10 μm aerodynamic diameter) fractions.

Table 2. Characteristics of PM-10 reference method samplers.

Sampler	Size ranges, μm	Inlet type	flow rate L/min	Filter size
Wedding PM-10	<10	cyclone	1133	203 mm x 254 mm
Andersen PM-10	<10	impactor	1133	203 mm x 254 mm
Andersen dichotomous	<2.5 and 2.5-10	impactor	16.7	37 mm diameter

Several field studies have been conducted to compare performances of the samplers shown in Table 2 (Rodes et al., 1985; Purdue et al., 1986; Hoffman et al., 1988). John (1988) evaluated data from Phoenix, AZ (Purdue et al., 1986) and found that measured PM-10 mass concentrations can be ranked by sampler as follows:

Wedding hi vol < Dichotomous sampler < Andersen hi vol, (1)

with deviations from dichotomous sampler results being as large as 30%. John (1988) attributed the higher Andersen values to bounce and reentrainment of particles in the impactor inlet — an effect that diminished when the impactor plate was coated with oil. He attributed the lower Wedding values to blocking of the airflow by buildup of collected particles in the cyclone — an effect that diminished when cyclone surfaces were cleaned daily. Two models of dichotomous samplers gave equivalent PM-10 values (fine and coarse fraction data were summed). When an oiled Andersen PM-10 hi vol and a daily-cleaned Wedding PM-10 hi vol were compared with a dichotomous sampler, the ranking in Equation (1) still applied, but average deviations were less than 13% (John, 1988; Hoffman et al., 1988). Consequently, oiling and cleaning of hi vol inlets have become a necessary part of the PM-10 measurement process (Purdue, 1988).

The dichotomous sampler's ability to collect particles in the fine and

coarse fractions is useful in receptor modeling because such size separation discriminates between particles generated by combustion and mechanical processes. Although it may seem that the flow rate in a dichotomous sampler is too low to collect sufficient sample for analysis, this is generally not the case because many analytical methods do not require large samples, and high-purity Teflon filters work best in a low-flow-rate sampler.

An automated device named "SCISAS" has been designed to collect up to six samples of particles in two size ranges for applications of receptor models to visual air quality in western United States (Rogers et al., 1988). Another sampler is the "Streaker", which collects a time-sequence of 1-mm by 8-mm samples on a strip of Nuclepore filter for element analysis by PIXE (Nelson, 1977); this sampler can be equipped with an impactor to remove particles larger than 10 μm.

3 Filter media

Filter media must be compatible with requirements of both the air sampler and analysis method. The characteristics of filter media commonly used in air sampling are shown in Table 3, and their compatibility with various air samplers and analysis methods is described in Table 4.

Because thin Teflon membrane is difficult to handle, it is either mounted on annular polymethylpentene rings and sold as Teflo, or it is mounted on porous Teflon mat and sold as Zefluor (Gelman Sciences, Ann Arbor, MI). Despite the 2-μm pore size, the efficiency is very high for particles as small as 0.03 μm (Liu et al., 1983). Ring-mounted Teflon filters are excellent for XRF because their low mass per unit area and high purity enable good detection limits to be obtained. An exception is Lot 225, which is contaminated with Pb (Cooper, 1988). Teflon filters are not very good for PIXE because of a γ-ray background due to interactions between the proton beam and the fluorine in the Teflon.

Table 3. Characteristics of several filter media used in aerosol sampling.

	0.3-μm Nuclepore	2-μm Ringed Teflon[d]	2-μm Teflon Zefluor[d]	Quartz Type QMA (Whatman)	Quartz Microquartz (Gelman)
Face velocity[a]	10.6	64.1	86.7		41.6
Mass/area[b], mg/cm^2	1.0	0.6	10.8	8.4	8.7
E(0.035 μm)[c], %	99.3	99.9	94.6		99.9
E(0.1 μm)[c], %	98.6	>99.9	99.0		99.7
E(0.3 μm)[c], %	>99.9	>99.9	99.9		>99.9

[a]Face velocity in cm/sec for pressure drop of 3 cm mercury.

[b]Mass per unit area for ringed Teflon filter does not include ring.

[c]Efficiency E(D) for particles of diameter D was measured by Liu et al. (1983).

[d]The tested Teflon filters were made by Ghia Corp., which no longer exists, but equivalent filters are now available from Gelman Corp. (Ann Arbor, MI).

Table 4. Compatibility of filter media with sampling and analysis methods.

	0.3-μm Nuclepore	Ringed Teflon	Zefluor	Quartz
Sampling				
PM-10 hi vol	poor	none	fair	excellent
Dichotomous	excellent	excellent	excellent	excellent
Resistance to clogging	poor	fair	fair	excellent
Analysis				
Gravimetric	good	good	good	fair-good[c]
XRF	good[a]	excellent	poor-fair[b]	poor
PIXE	excellent	fair	poor	poor
INAA	good	excellent	excellent	difficult
ICP	good	excellent	excellent	good
Pyrolysis	none	none	none	fair-good[d]

[a]Nuclepore sometimes contains troublesome amounts of Si and Br.

[b]Zefluor is fair for XRF only if sample is collected on the membrane side.

[c]Quartz is good for gravimetric analysis when RH is properly controlled.

[d]Because quartz filters adsorb carbon vapor, quartz filters are good for particulate carbon only if an appropriate correction is made for adsorbed carbon.

The Teflon mat in Zefluor can cause problems for XRF and wet chemical analysis. The mat adds to the total mass per unit area, which increases X-ray blank levels and raises the minimum detection limits by about a factor of 3. Also, if particles are sampled on the mat side, they are collected deep within its structure, which attenuates soft X rays from light elements such as Al, Si, S and K and causes a large, difficult to determine bias. The membrane side of Zefluor is not easily discerned at first, but personnel can locate it with training and a magnifying glass. Postsampling validation by examination with a light microscope (100 to 400X) is needed to verify that the deposits are on the proper side. Another reason to require that particles be collected on the membrane side is that some wet extraction procedures do not efficiently extract particles imbedded in the Teflon mat.

Zefluor filters are available that will fit in hi vol samplers, and Table 3 indicates that they have low flow resistance when clean. However, the Teflon membrane in Zefluor clogs so quickly that after a few hours of sampling, the pump in a typical hi vol cannot maintain a steady flow rate. Clogging is less of a problem with Teflon membrane in a dichotomous sampler, because its pump can deliver a low but constant flow rate for fine particle loadings up to 150 $\mu g/cm^2$ on a dry weight basis. However, higher fine particle mass concentrations in humid air can cause the flow-rate controller in a dichotomous sampler to fail to maintain constant flow. Quartz filters are much less prone to clogging than Teflon and are therefore best to use in hi vol samplers. However, quartz filters have high concentrations of Si, Ca, Fe and other elements and are not good for XRF and INAA. A further complication for XRF is that a quartz filter collects particles within its volume, which causes soft X rays from light elements to be attenuated by amounts that are difficult to determine. Quartz filters are best analyzed for trace elements by extracting the sample in strong acids. However,

an extraction procedure designed not to dissolve the quartz filter may not be efficient for elements in silicate minerals (Al, Si, Ti and Fe).

Whatman 41 is a type of cellulose filter that has high loading capacity, works well in a hi vol sampler, and has very low blank values (Dams et al., 1972). Laboratory tests show that these filters have efficiencies of 43, 52 and 92% for 0.03-, 0.1- and 0.3-μm-diameter particles, respectively (Liu et al., 1983). Although such low efficiencies exclude this filter for monitoring to meet the U. S. PM-10 standard, Lowenthal and Rahn (1987) demonstrate that the efficiency of Whatman 41 filters exceeds 90% for 24-hour atmospheric samples.

4 Mass and elemental analysis methods

4.1 Sample handling and transport. When quartz filters are folded, they splinter, and their tare masses change. To maintain stable tare masses and avoid particle loss, quartz filters should be transported from sampling site to laboratory in cassettes oriented deposit-side-up. After mass measurements are completed, quartz filters may be folded to avoid particle loss during further shipment or storage.

Ring-mounted Teflon filters are held in circular cassettes in a dichotomous sampler and may be stored in those cassettes in petri dishes before and after sampling. To avoid particle loss, samples should be deposit-side-up during transport from field to laboratory. When filters are shipped by mail, one has little control over orientation, but losses can be greatly reduced by applying a thin layer of mineral oil (25 $\mu g/cm^2$) to coarse fraction filters in the laboratory before sampling (Dzubay and Barber, 1983). No oil is needed for fine particles. Accurate gravimetric analysis is possible if the mineral oil is applied before tare mass is determined. Small amounts of mineral oil do not interfere with XRF analyses.

4.2 **Gravimetric analysis.** Mass is determined by weighing each filter before and after sampling. Filters are stored in an atmosphere of 20 to 45% relative humidity (RH) for 24 hours before each mass measurement. Because the mass of a quartz filter is sensitive to relative humidity, RH must be constant to ±5% between tare and final mass determinations. Ring-mounted Teflon filters require a microbalance with 1-μg precision. Electrostatic charge, which accumulates on Teflon filters, must be removed by exposing each side of a filter for a few seconds to alpha particle radiation from a ^{210}Po source (Model 2U500 Staticmaster, Nuclear Products Co., El Monte, CA). If a wire balance pan is used a ^{210}Po source can be mounted below the pan so that charge neutralization occurs while each filter is weighed. Because the half-life of ^{210}Po is 138 days, the source should be replaced at least every 12 months.

4.3 **X-ray fluorescence spectrometers and sample requirements.** In XRF analysis a beam of X rays irradiates the sample and causes elements to emit characteristic X rays, which are detected by a solid state detector or a crystal spectrometer. The X-ray source may be direct emissions from an X-ray tube, or it may be the nearly monochromatic X rays from a secondary target irradiated by an X-ray tube.

Figure 1 shows an X-ray spectrum for fine particles on a Teflon filter irradiated by a Mo secondary target. The detector is a silicon diode (1-cm diam, 0.3 cm-thick) containing small amounts of lithium. The detector and related electronic components constitute an EDXRF spectrometer, which enables several elements to be determined simultaneously (Jaklevic et al., 1981). Optimum detection limits for a wide range of elements are obtained when several different secondary targets and X-ray tube voltages are used to analyze each sample. In WDXRF analysis, a crystal spectrometer is used to measure elements sequentially (Wagman et al., 1977). In PIXE analysis, a beam of protons or alpha particles

excites the sample (Nelson, 1977).

Table 5 compares element concentrations measured in Camden, NJ, and Great Smoky Mountains with 2σ measurement precision for EDXRF, WDXRF, and PIXE. The units for 2σ in Table 5 are ng/cm^2 and are equivalent to $ng\backslash m^3$ for a 7-hour sample collected at 16 L/min on a 6.5-cm^2 area in a dichotomous sampler. The 2σ data pertain to analysis of low element concentrations on a blank filter and include propagation of error due to statistical fluctuations in the X-ray background of element measured and interfering elements. Much of the background is due to X-ray scattering by the filter.

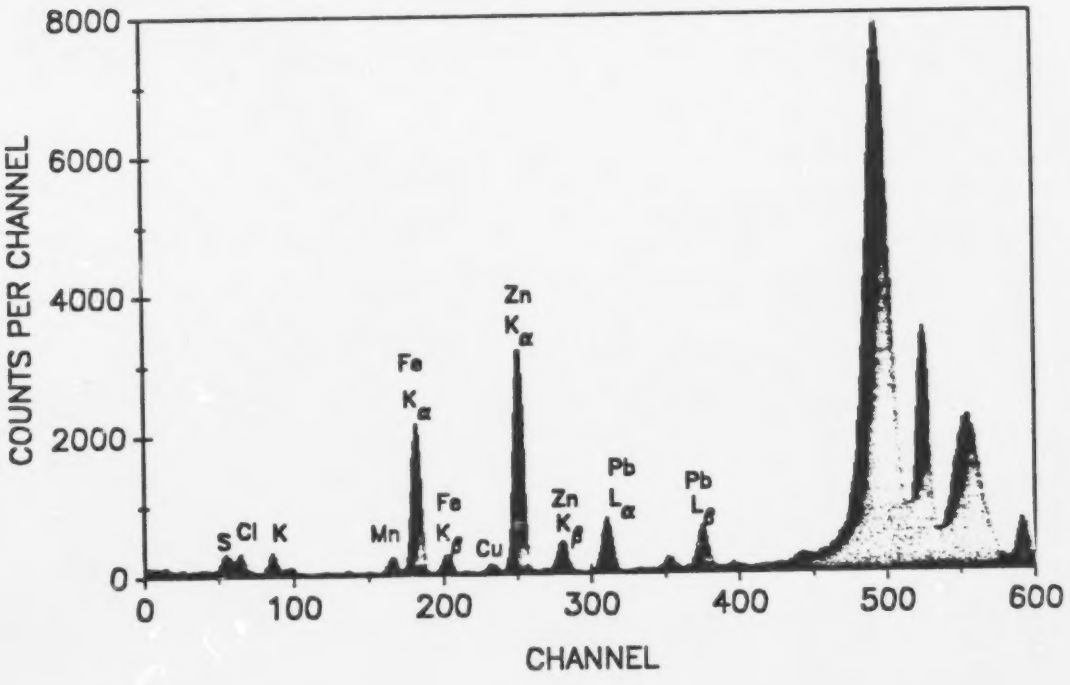

Figure 1. EDXRF spectrum of fine particle sample using excitation by a Mo secondary target. X rays above channel 450 are due to the Mo target.

Table 5. Typical atmospheric concentrations and 2σ measurement precision.

	Concentrations, ng/m^3				2σ measurement precision[a] in ng/cm^2			
	Camden, NJ[b]		Elkmont, TN[c]		EDXRF[d]	EDXRF[e]	WDXRF[f]	PIXE[g]
	Fine	Coarse	Fine	Coarse	DRI	EPA	EPA	EAC
Al	53	550	20	195	13	101	4	24
Si	103	1610	38	580	6	36	7	20
S	4200	230	3700	200	3	13	5	15
Cl	3	69	<10	7	7	10	26	14
K	101	151	40	110	4 (3)	8 (5)	13	(10)
Ca	40	360	16	190	4 (3)	10 (5)	2	(9)
Ti	15	65	<2	<2	18 (2)	14 (3)	2	(7)
V	13	7	<2	<2	7 (1)	5 (3)	8	(6)
Cr	2	3			2	2	26	2
Mn	6	11			1	2	23	2
Fe	91	490	28	120	1	4	9	1
Ni	11	4	1	2	1	2	9	1
Zn	82	30	2	<1	1	1	11	1
As	1	0	2	<1	2	2	13	1
Se	2	0	2	<1	1	1	16	1
Br	29	15	18	5	1	1	38	3
Cd	2	0			9	9	2	46
Sn	5	1			14	16	11	75
Sb	79	181			16	14	5	99
Ba	<30	<30			59	33	7	(24)
Pb	249	54	97	14	3	3	94	4

[a]Filter medium is 2-μm pore size ringed Teflon for XRF and Nuclepore for PIXE. Data in parentheses represent assumption of no interferences between K_α X rays from K, Ca, Ti and V and L_α and L_β X rays from Cd, Sn, Sb and Ba.

[b]One-month average for summer 1982 (Dzubay et al., 1988).

[c]Data for September 1978 in Great Smoky Mountains (Stevens et al., 1980).

[d]Desert Research Institute (DRI) excitation conditions (and X-ray tube voltage) are cellulose-filtered direct excitation (8 kV) for Al - S; Ti secondary target (30 kV) for Cl - Ca; Ge secondary target (30 kV) for Ti - Zn; Rh-filtered direct excitation (35 kV) for As - Mo and Pb; Mo-filtered direct excitation (60 kV) for Pd - La. Analysis time is 18 min. (Frazier, 1989)

[e]Secondary targets (and X-ray tube voltages) are Ti (41 kV) for Al - Ca; Co (41 kV) for S - Mn; Mo (50 kV) for Fe - Sr and Pb; Sm (66 kV) for Sr - Ba. Analysis time is 14 min. (Kellogg, 1989)

[f]Excitation by Cr X-ray tube operated at 54 kV and 44 mA; Al, Si, P, S, Cl, K, Br, Sr, Mo, Cd and Pb are determined simultaneously in 100 seconds using fixed channels. All other listed elements are determined sequentially by scanning the X-ray spectrum for 20 sec per element. (Kellogg, 1989)

[g]Proton beam energy is 3.2 MeV; analysis time is 6 min. Data are from brochure by Element Analysis Corporation (EAC), Tallahassee, FL.

In EDXRF analysis Cd, Sn, Sb and Ba are best determined by their K_α X rays, which are free of interferences, but the lower energy L_α and L_β X rays from those elements interfere with the K_α and K_β X rays measured for K, Ca, Ti and V. In most EDXRF analyses the needed interference corrections are based on Cd, Sn, Sb and Ba concentrations, which are measured poorly by XRF, and this causes the interference corrections to have poor precision. Table 5 shows two sets of precision data for K, Ca, Ti and V. The larger values are more realistic, for they include the precision with which the interference corrections can be made. The smaller values (in parentheses) are based on the assumption that interfering elements are absent.

Although XRF is considered to be nondestructive, this is not strictly true. During XRF analysis, the sample must be in vacuum or in helium to eliminate air and argon, which attenuate and interfere with X rays from light elements. If a sulfuric acid sample is analyzed in vacuum, loss by volatilization may occur. Also, during WDXRF analysis a sample receives a large radiation dose, which makes the filter brittle and may volatilize Br and Cl. Radiation damage during EDXRF analysis is negligible. Data in Table 5 suggest that detection limits can be improved if a sample is first analyzed by EDXRF for all elements and then by WDXRF for Al, Ti, Cd, Sn, Sb and Ba. By limiting WDXRF to those few elements, precision can be improved by using longer counting time per element while total radiation dose is reduced. The precision of XRF varies inversely as the square root of counting time, so precision improves by a factor of 2 for every factor of 4 increase in counting time.

The sensitivity profile for a typical XRF analyzer is nonuniform across a sample's diameter. For such an instrument, quantitative analysis is possible only if the standards and samples have identical deposit profiles. This requirement is satisfied most easily if both sample and standards have uniform

deposit profiles. Thus, most cascade impactor samples, which are nonuniform, are unsuitable for XRF. An exception is the micro orifice impactor, which deposits size-fractionated particles uniformly on surfaces (Hasan and Dzubay, 1987). Uniformity of deposit profile is less a concern for PIXE because the proton beam used by that method can be made small and uniform.

4.4 Quantitative XRF analysis. In an X-ray spectrum such as the one shown in Figure 1, peak areas are proportional to the concentrations of the elements they represent. One method to determine peak areas in a multielement spectrum is to use a least squares fitting method to represent the spectrum as a superposition of spectra for pure element standards and a blank filter (Arinc et al., 1977). This method automatically determines the peak area for each element in the presence of background and interferences, and it provides a good way to estimate measurement precision. Another method is to sum the spectrum over specified intervals to determine peak areas and background; arithmetic corrections are made to account for interferences.

A practical way to relate spectral peak areas to element concentrations is to use thin, single element standards and make mathematical correction for attenuation of X rays within unknown samples (Dzubay et al., 1987). A single concentration is needed for each element if it is in the instrument's linear range and if background is subtracted appropriately. A seemingly good alternative is to use multielement standards that exactly duplicate the attenuation effects of all unknown samples, but such standards do not exist. Reliable single element standards are made by Micromatter Co. (Deer Harbor, WA) by vacuum deposition of pure metals or compounds onto Nuclepore filters. Deposit masses are determined gravimetrically and range typically from 20 to 80 $\mu g/cm^2$. Another type of standard that is rugged and reliable is polymer film with known

amounts of organometallic compounds; element concentrations range from 2 to 12 $\mu g/cm^2$ in the polymer (Dzubay et al., 1987). The substrates for standards and samples need not be identical if background is properly subtracted from the spectra for standards and unknowns.

Because no standard has perfect accuracy, one should not rely on any single standard. We use a semiempirical model to derive a calibration constant for each element based on data for all standards and all elements. This approach not only improves the calibration for elements that have accurate standards, but it provides accurate calibration by interpolation for P, Ga, As, Se and Br, which have poor standards because of volatility or uncertain stoichiometry. Results are plotted in Figure 2.

The National Institute of Standards (NIST, formerly NBS) has developed standard reference materials (SRMs) for XRF which are thin, uniform glass

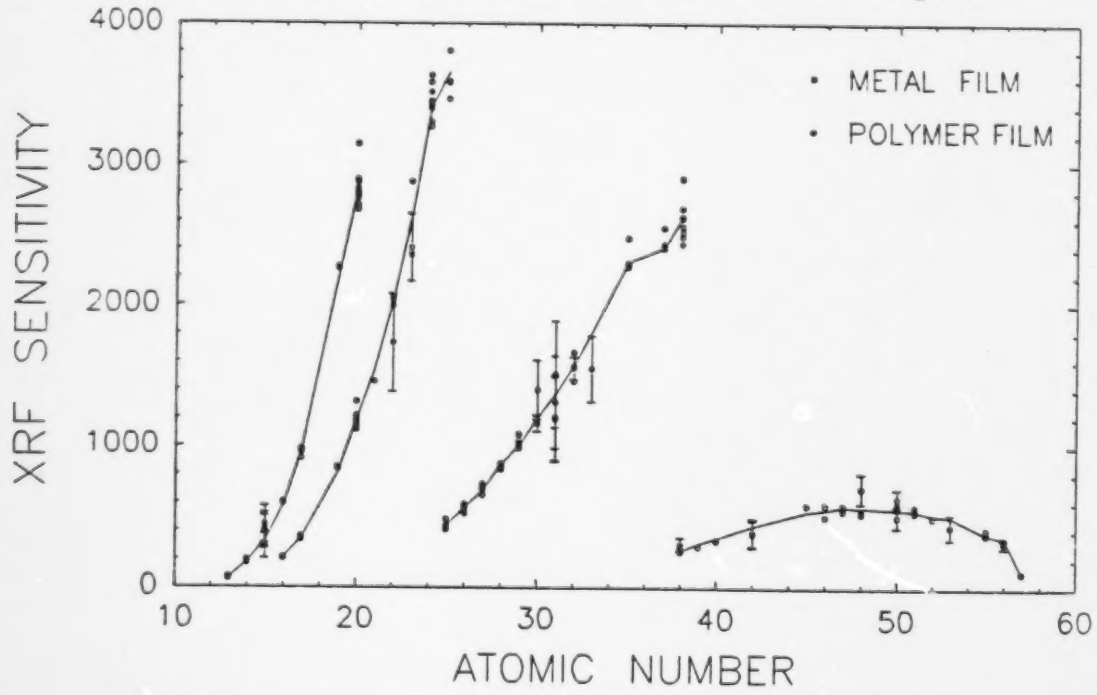

Figure 2. XRF calibration constants based on semiempirical model applied to 203 different polymer film and evaporated film standards. (Many data points close to the fitted line overlap each other and are therefore not seen.)

deposits on Nuclepore filters. Certified elements in SRM 1832 are Al, Si, Ca,V, Mn, Co and Cu; certified elements in SRM 1833 are Si, K, Ti, Fe, Zn and Pb. We use these standards to validate the calibration constants derived from thin film standards and to provide daily quality control checks on accuracy of EDXRF data. Fine particles are typically collected as layers of particles on the surface of a membrane filter (Loo et al., 1977), and reliable corrections for attenuation can be made assuming a uniform deposit. The correction for fine particles is usually small since the membrane filter will clog before enough mass is collected to cause large attenuation.

Coarse particles are collected mainly as a monolayer, and the correction for attenuation is made by assuming that each particle is a sphere (Dzubay and Nelson, 1975). Such corrections are uncertain when size distributions and compositions of individual coarse particles are unknown. Thus, we base the attenuation correction on the range of results calculated for a wide variety of compositions and size distributions. Table 6 shows attenuation correction factors calculated for excitation by Ti, Co and Mo secondary targets. Uncertainty is largest for Al, Si and P, which emit soft X rays that are easily absorbed within each particle. The attenuation correction factor for Al excited by Ti X rays is 0.56 ± 0.15 and represents the diverse values 0.41, 0.58 and 0.70 for almandine, muscovite and kaolinite, respectively. For samples collected by using a PM-10 inlet, the dependence on size distribution is not large. For example, the attenuation factors for muscovite are 0.58 and 0.54 for a size distribution with geometric standard deviation of 2 and mass median aerodynamic diameters of 10 and 15 μm, respectively.

When XRF data are reported, both concentrations and uncertainties should be reported. Measurement uncertainty due to the random nature of counting X rays can be derived from Poisson statistics and should include count rates due to background and interfering elements as well as the element itself. Some

Table 6. Attenuation correction factors for XRF analysis of coarse particles[a].

Element analyzed	Ti target 4.5-keV excitation	Co target 7-keV excitation	Mo target 18-keV excitation
Al	0.56 ± 0.15	0.59 ± 0.16	
Si	0.57 ± 0.13	0.61 ± 0.12	
P	0.65 ± 0.20	0.68 ± 0.19	
S	0.81 ± 0.13	0.85 ± 0.10	
Cl	0.81 ± 0.10	0.84 ± 0.09	
K	0.84 ± 0.10	0.88 ± 0.08	0.90 ± 0.08
Ca	0.81 ± 0.05	0.88 ± 0.04	0.91 ± 0.04
Ti		0.81 ± 0.08	0.90 ± 0.06
V		0.87 ± 0.08	0.92 ± 0.05
Cr		0.87 ± 0.08	0.93 ± 0.05
Mn		0.87 ± 0.08	0.94 ± 0.05
Fe			0.95 ± 0.04
Ni			0.93 ± 0.05
Zn			0.93 ± 0.05

[a]Size range is 2.5- to 10-μm aerodynamic equivalent diameter.

investigators also include systematic error. If the true concentration is zero, negative and positive values are equally probable because background, which has random error, is subtracted to obtain a final value. Thus, -1.1 ± 0.8 ng/m^3 is a valid result that is not significantly different from zero and does not imply a meaningless negative concentration. It is common to replace negative values with zero or a positive number, but that introduces bias that complicates use of the data to compute statistical parameters.

4.5 Instrumental neutron activation analysis. In INAA a sample absorbs thermal neutrons in a nuclear reactor and undergoes nuclear transitions that result in γ-ray emissions characteristic of nuclei in the sample (Zoller and Gordon, 1970; Dams et al., 1972; Ondov et al., 1975). After samples are withdrawn from the reactor, they are allowed to "cool" to diminish activities of short-lived interfering isotopes, and γ-ray spectra are obtained with lithium-drifted or intrinsic germanium detectors. Near optimal results are obtained when

irradiation, cooling and counting periods are about equal to the half life of the isotope measured. Because half-lives of isotopes of interest range from 2 min to more than 12 years, it is not practical to satisfy such criteria for every element, but very good results can be obtained for more than 25 elements if two irradiation periods and four counting periods are used as shown in Table 7.

Gordon et al. (1984) compare detection limits for INAA with typical ranges of element concentrations in the atmosphere in order to predict which elements

Table 7. Typical INAA analysis conditions and performance[a].

	Group 1	Group 2	Group 3	Group 4
Product half-life	<12 min	12-1440 min	1-3 d	>3 d
Irradiation time	5 min	5 min	4 h	4 h
Cooling time	3-6 min	15 min	2-5 d	20-30 d
Counting time	6 min	30 min	1-4 h	2-24 h
	+ Mg (^{27}Mg)	+++ Na (^{24}Na)		+++ Sc (^{46}Sc)
	+++ Al (^{28}Al)	+++ Cl (^{38}Cl)		+++ Cr (^{51}Cr)
	+ S (^{37}S)	+++ K (^{42}K)		+++ Fe (^{59}Fe)
	++ Ca (^{49}Ca)	+++ Mn (^{56}Mn)	+++ As (^{76}As)	+++ Co (^{60}Co)
	++ Ti (^{51}Ti)	+ Ga (^{72}Ga)	++ Br (^{82}Br)	Ni (^{58}Co)
	+++ V (^{52}V)	++ Br (^{80}Br)	+ Mo (^{99}Mo)	+++ Zn (^{65}Zn)
	+ Cu (^{66}Cu)	+ Br (^{80m}Br)	++ Cd (^{115}In)	+++ Se (^{75}Se)
		+ Sr (^{87m}Sr)	+ Sb (^{122}Sb)	++ Rb (^{86}Rb)
		+ In (^{116m}In)	+++ La (^{140}La)	+ Zr (^{95}Zr)
		++ I (^{128}I)	+++ Sm (^{153}Sm)	+ Ag (^{110m}Ag)
		+ Ba (^{139}Ba)	++ W (^{187}W)	+++ Sb (^{124}Sb)
		+ Dy (^{165}Dy)	+ Au (^{198}Au)	++ Cs (^{134}Cs)
		++ W (^{187}W)		+ Ba (^{131}Ba)
				+++ Ce (^{141}Ce)
				++ Eu (^{152}Eu)
				+ Tb (^{160}Tb)
				+ Yb (^{169}Yb)
				++ Lu (^{177}Lu)
				++ Hf (^{181}Hf)
				++ Ta (^{182}Ta)
				++ Th (^{233}Pa)

[a]The isotope measured for each element is shown in parentheses. Performance, based on results of Gordon et al. (1984) for analysis of St. Louis samples, is represented as follows:

+++ elements strongly measured in fine and coarse fractions.
++ elements strongly measured in fine or coarse fraction.
+ elements moderately measured in fine or coarse fraction.

can be measured. Gordon et al. also characterize INAA by noting whether an element was measured strongly or moderately in aerosol samples collected in St. Louis, and their results are summarized in Table 7. The results are based on the NBS heavy water moderated reactor at Gaithersburg, MD. The neutron flux was 2 to 5 x 10^{13} cm^2/sec. These results illustrate what can be measured by INAA, but they may not generally apply to other laboratories because each laboratory optimizes its measurement system in a different way. For example, there are fewer interferences among elements if a heavy water reactor is used, but Ni can be detected only if a light water reactor is used (Gordon et al., 1984).

4.6 **Element analysis by optical spectroscopy.** Elements extracted from filters can be measured by AA or ICP. A typical AA instrument can analyze only one element at a time, although newer instruments can analyze two or even four elements simultaneously. The ICP system used by EPA to determine trace elements in hi vol samples analyzes 48 elements per sample simultaneously (Cummings et al., 1984). Harper et al. (1983) have developed an optimized method that extracts more of the particulate matter and less of the contaminants in a glass fiber filter than was possible with an earlier EPA method. In the optimized method, a 2.5- x 20-cm portion of filter is extracted in a heated ultrasonic bath in 2.2 M HCl and 1 M HNO_3 (Harper et al., 1983).

Table 8 compares ICP results for 195 hi vol samples extracted by the optimized and earlier extraction methods. In every case the optimized method has equal or improved extraction efficiency. Several elements (Ti, V, Mn, Fe, Cu, Zn and Pb) were detected in almost all of the samples, but concentrations of other elements (Cr, Co, Ni, As, Mo, Cd and Ba) were significantly greater than the blank in less than 30% of the samples. Newer, more sensitive ICP instruments applied to purer quartz filters may yield better detection for more elements.

Table 8. Performance of ICP for analysis of ambient samples and standard reference material[a].

	Optimized vs earlier extraction method for 195 hi vol samples			Extraction efficiency for NBS SRM 1648 (Urban particulate matter standard)	
	number detected	slope[b]	correlation coefficient	Mean % recovery	Relative standard deviation, %
Ti	192	0.33	0.87	12	5.0
V	138	0.91	1.00	79	1.9
Cr	27	0.95	0.93	23	1.4
Mn	195	0.91	0.98	88	1.6
Fe	175	0.34	0.87	68	1.4
Co	0			96	5.4
Ni	33	0.88	0.98	90	9.0
Cu	194	0.92	0.99	100	1.4
Zn	170	1.13	0.73	97	3.8
As	15	1.00	0.99	130	2.2
Mo	14	0.88	0.95		
Cd	19	0.95	1.00	114	8.5
Ba	51	0.17	0.49	80	0.8
Pb	192	1.00	1.00	95	1.1

[a]Results reported by Harper et al. (1983)

[b]Regression results for: earlier method = intercept + slope x optimized method

Table 8 also shows extraction efficiencies for elements in a standard reference material for urban particulate matter. Extraction is quantitative for 10 elements, but Ti and Cr are not extracted efficiently. The acids used in the extraction are not expected to provide quantitative recovery of elements in silicate minerals. Thus, if ICP is used to provide data for receptor models, it may be necessary also to use INAA to determine elements that are difficult to extract. Although the Na in glass fiber filters causes high background that impairs INAA performance, Lambert and Wilshire (1979) were able to obtain reliable INAA results for several elements.

Table 9 shows typical 2σ detection limits for a modern ICP instrument. Data in Tables 5 and 9 indicate that ICP is superior to XRF for Li, Be, B, Na,

Mg, Ca, Ti, V, Mn, Sr, Y, Zr, Ag, Cd and Ba collected in a dichotomous sampler. However, to take full advantage of the capabilities of ICP for analyzing Teflon filters, it will be necessary to develop an extraction procedure that does not introduce contamination and is quantitative for all elements.

Table 9. Limits of detection for ICP instrument in ng/mL of sample extract[a,b].

Li	0.8	Ca	0.07	Se	14.
Be	0.13	Ti	0.4	Sr	0.07
B	1.1	V	0.8	Y	0.5
Na	5.0	Cr	1.0	Zr	2.5
Mg	0.07	Mn	0.2	Ag	1.2
Al	4.7	Fe	1.0	Cd	0.6
Si	3.3	Cu	0.9	Sn	6.7
P	13.	Ni	2.7	Sb	7.4
S	20.	Zn	0.5	Ba	0.7
K	20.	As	7.4	Pb	10.

[a]Model JY 70 Plus by Instruments S. A. Inc., Optical Systems Div., Edison, NJ.

[b]The tabulated data are equivalent to ng/m^3 for 10-hour air samples collected in a dichotomous sampler at 16.7 L/min and extracted in 10 mL of solution.

4.7 Carbon analysis. Volatilizable carbon (C_v) and nonvolatilizable carbon (C_{nv}) on quartz filters can be determined by pyrolysis. To remove carbon contamination before sampling, quartz filters are heated in air at 700°C for several hours and stored in aluminum-foil-lined petri dishes. During analysis, C_v is determined first by heating the sample to temperature T_1 in pure helium and measuring volatilized carbon as CO_2 by infrared spectroscopy after oxidation or as methane by flame ionization after reduction. Then, C_{nv} is determined by heating the sample to temperature T_2 in a helium-oxygen mixture and measuring oxidized carbon. Pyrolysis temperatures used by various laboratories are in the ranges $350 < T_1 < 950$°C and $600 < T_2 < 950$°C (Hering et al., 1988). To account for charring so that C_v and C_{nv} can be related to organic and elemental carbon, some investigators measure light absorption as samples are heated during

pyrolysis (Johnson et al. 1981).

Several laboratories participated in a field study to compare methods for measuring carbon (Hering et al., 1988). When participants analyzed identical samples, excellent agreement was obtained for total carbon (C_v + C_{nv}), but results were variable for C_{nv}, which comprised about 25% of total carbon (Hering et al., 1988). Larger variability for both C_v and C_{nv} was obtained when both sampling and analysis methods were compared. Some of the variability was attributed to adsorption of organic vapors by quartz filters.

A correction for adsorption of organic vapors can be made if carbon is analyzed on two quartz filters that have been sampled in series. One approach is to use two quartz filters in series in the same airstream. Another approach is to collect carbon on quartz filters in two parallel sampling streams where quartz is preceded by a Teflon filter in one of the streams. With either approach, particulate carbon is calculated as the difference between amounts of carbon on the two quartz filters. Field study results showed that quartz behind quartz collected less organic carbon vapor than quartz behind Teflon (Hering et al., 1988), which indicates that quartz collects more organic carbon vapors than Teflon. Until it becomes known which approach is best, data for C_v and C_{nv} should be used with caution. If one must use such data in a chemical mass balance, some of the ambiguity can be avoided if the same sampling protocol and laboratory are used to analyze all source signature and ambient aerosol samples. That may preclude the use of carbon data in source signature libraries.

4.8 ^{14}C analysis. Cosmic rays continuously bombard atoms in the upper atmosphere and produce ^{14}C, a radioactive isotope with 5730-year half-life. Carbon atoms containing this isotope are oxidized in the atmosphere to form CO_2 that becomes incorporated into living matter. Although fossil fuel originated

as living matter, its ^{14}C has completely decayed away, and it contains only stable isotopes ^{12}C and ^{13}C. Thus, through measurement of the $^{14}C/^{13}C$ ratio, fossil fuel combustion products can be distinguished from modern carbon-containing particles such as pollen and combustion products of wood and paper. In past years, ^{14}C in aerosol samples was measured by oxidizing the sample to CO_2 and incorporating it into a gas-filled radiation counting tube (Currie, 1979). About 5 mg of carbon was needed for analysis, an amount easily collected in a hi vol sampler. Cooper et al. (1981) determined ^{14}C in <2.5-μm particles collected in a hi vol equipped with an impactor inlet and were able to estimate contributions due to slash burning and field burning. Lewis et al. (1988) collected <2.5-μm particles during winter in Albuquerque and demonstrated that ^{14}C in extractable organic matter was proportional to the amount of wood smoke.

Accelerator mass spectrometry enables ^{14}C atoms to be measured directly. An AMS instrument consists of a sample ionizer, a tandem Van de Graaff that accelerates carbon ions to an energy of 12 MeV, a magnetic separator that selects mass 13 and 14 ions, and a particle detector that identifies and counts ^{13}C and ^{14}C ions. Verkouteren et al. (1987) have developed a sample preparation technique that enables ^{14}C to be determined by AMS in samples that have 10 to 800 μg of carbon. This technique is sensitive enough to analyze 24-hour samples collected in a dichotomous sampler. Because there is a limited number of laboratories capable of AMS analysis, there are large backlogs, and it is difficult to obtain timely analysis.

5 Ionic analysis of particles collected on filters

5.1 Extraction. Analysis of ionic species collected on a filter requires extraction of the ions into an aqueous solution. Quantitative extraction of soluble ions on Teflon filters requires the use of ethanol to overcome the

hydrophobic nature of Teflon. The following procedure has been developed for 37- and 47-mm Teflon filters and is similar to one used by Koutrakis et al. (1988a): Immediately after sampling, a filter is placed in an extraction vial (vial diameter must exceed filter diameter) containing 10 mL of extraction solution and stored in the dark at 5°C to retard bacteria growth until time of analysis. When ready for analysis, the filter is removed from its vial, and 100 μL of ethanol is pipetted onto the filter to wet it uniformly. The filter is immersed again in the vial and agitated in an ultrasonic bath for 15 min. If H^+ is to be measured, the extraction solution should be 10^{-4} M $HClO_4$, which keeps CO_2 and weak acids from disassociating. Otherwise, the extraction solution may be either deionized water or the eluent solution used in ion chromatography.

5.2 Ion chromatography. Ion chromatography is a technique for separation and automatic measurement of ions in solution (Mulik and Sawicki, 1979; Gjerde and Fritz, 1987). Measurement consists of injecting a sample into an eluent that passes through an ion exchange column followed by a suppressor unit and a conductivity detector. For anion analysis, the eluent typically consists of a mixture of 2.8 mM $NaHCO_3$ and 2.2 mM Na_2CO_3 (Gjerde and Fritz, 1987). The ion exchange column retards the flow of sample by a different amount of time for each ion, and the conductivity detector responds linearly to each anion. The suppressor unit eliminates the high conductivity of the eluent by converting it to H_2CO_3. The separation characteristics of the ion exchange column can be optimized for certain ions by adjusting the ratio of $NaHCO_3$ to Na_2CO_3 in the eluent (Speitel et al., 1979). Ion chromatography can also be used to measure cations (Gjerde and Fritz, 1987).

Analytical detection limits below 1 μg/mL are obtained routinely by using an instrument made by Dionex Corp. (Sunnyvale, CA). This corresponds to

detection limits below 0.5 $\mu g/m^3$ for a 24-hour fine particle sample collected at 15 L/min and extracted in 10 mL. Anions routinely measured in aerosol samples include sulfate and nitrate. Additional anions seen in some samples include bromide, chloride, nitrite, sulfite, formate and acetate. An automated ion chromatograph can analyze three to five samples per hour. Ethanol, which serves as a wetting agent in the extraction, is unlikely to damage the IC column. Reasonably long life for the ion exchange column can be obtained if an upstream filter is used to remove bacteria in the eluent and if a relatively fresh "guard column" is used upstream to remove polyvalent metals that might contaminate the main column (Gjerde and Fritz, 1987).

5.3 **Ion analysis by colorimetry.** Sulfate, nitrite, nitrate and ammonium in sample extracts can be analyzed rapidly by colorimetry. Sulfate is determined by measuring absorbance at 460 nm in a sample processed as follows: (1) passage through a cation exchange column to remove interferences, (2) reaction with barium chloride in acidic solution to form barium sulfate, (3) reaction of excess barium with methylthymol blue in alkaline solution to form a blue chelate. Nitrite is determined by adding an acid and sulfanilamide to the extraction solution to form a soluble dye that is measured by absorbance at 520 nm. Nitrate is determined similarly after it is reduced by a copper catalyst to nitrite in an alkaline solution of hydrazine sulfate. Ammonium is determined by measuring absorbance at 660 nm of a blue dye formed by reaction of ammonium with sodium phenoxide followed by addition of sodium hypochlorite. Interfering calcium and magnesium ions are removed by complexing with EDTA. An automated "TRAACS" colorimetric instrument by Technicon Industries can analyze up to 40 unknowns plus 30 standards per hour, which is considerably faster than the 3 to 5 per hour capability of an ion chromatograph.

5.4 Hydrogen ion measurement. Stevens *et al*. (1978) describe a Gran titration procedure by which H^+ from strong acid is determined from a plot of pH vs amount of NaOH titrant. As explained in Section 5.1, the extraction solution should contain $HClO_4$, but the portion analyzed for H^+ should also contain 0.04 M of KCl in order to increase the ionic strength and speed the response of the pH meter. Koutrakis *et al*. (1988a) deduce H^+ concentration from a single pH measurement without the need for a Gran titration. Such measurements determine strong acid because the $HClO_4$ prevents disassociation of weak acids.

5.5 Artifacts in measurement of ionic species. Although techniques described above are useful for determining ions collected in a PM-10 sampler, three types of artifacts can cause measured ions not to represent atmospheric particles: (1) filter artifacts, (2) reactions between gases and particles, and (3) reactions among particles.

Alkalinity of glass fiber filters can cause gaseous sulfur and nitrogen compounds to react and produce sulfate and nitrate artifacts. Such filter artifacts are minimal for Teflon filters or the low-alkalinity quartz filters required for PM-10 sampling.

Two kinds of reactions between gases and particles can alter the aerosol composition. (a) Acidic gases can react with alkaline particles, and (b) ammonia gas can react with acidic particles. Such reactions can occur in the atmosphere or on the filter. Examples are

$$2HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \uparrow \quad (2)$$

$$2HCl + MgCO_3 \rightarrow MgCl_2 + H_2O + CO_2 \uparrow \quad (3)$$

$$HNO_3 + NaCl \rightarrow NaNO_3 + HCl \uparrow \quad (4)$$

$$NH_3 + NH_4HSO_4 \rightarrow (NH_4)_2SO_4 \quad (5)$$

Reaction (2) can explain the occurrence in Camden, NJ, of nitrate in coarse particles, which contain calcium carbonate (Dzubay et al., 1988). Reaction (5) can cause hydrogen ion collected on a filter to be neutralized by ambient ammonia during sampling and analysis. Stevens et al. (1978) prevented neutralization by ammonia during sampling by using a diffusion denuder to remove ammonia upstream of the filter, and Koutrakis et al. (1988a) developed a procedure for preventing neutralization in the laboratory during storage and analysis.

Particles collected on a filter can also react with each other. This is especially true for fine particles, which can liquify and coalesce if they are hygroscopic and the relative humidity is high (Mamane and Dzubay, 1988). If both acid sulfate and anions of volatile acids are present, reactions such as the following can occur:

$$H_2SO_4 + 2NH_4NO_3 \rightarrow (NH_4)_2SO_4 + 2HNO_3 \uparrow \quad (6)$$

$$NH_4HSO_4 + NH_4NO_3 \rightarrow (NH_4)_2SO_4 + HNO_3 \uparrow \quad (7)$$

$$NH_4HSO_4 + NaNO_3 \rightarrow NH_4NaSO_4 + HNO_3 \uparrow \quad (8)$$

$$NH_4HSO_4 + NaCl \rightarrow NH_4NaSO_4 + HCL \uparrow \quad (9)$$

$$NH_4HSO_4 + CH_3COONa \rightarrow NH_4NaSO_4 + CH_3COOH \uparrow \quad (10)$$

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \uparrow \quad (11)$$

Because acidic sulfate is abundant in many parts of United States (Stevens et al., 1978; Stevens et al., 1980; Koutrakis et al., 1988a), reactions (7-11) can cause loss of hydrogen ion, nitrate, halides and salts of organic acids. Reaction (6) was observed in laboratory studies (Harker et al., 1977), and Slater et al. (1989) demonstrated significant loss of H^+ on ambient samples collected during winter in eastern United States. Reaction (11) expresses the fact that ammonium nitrate can decompose. All of these reactions indicate that, except for sulfate and metallic ions, ions measured on a filter may not represent the

ionic composition of atmospheric particles.

5.6 Diffusion denuder systems for measuring gases and particles. The artifacts described in Section 5.5 may be minimized through the use of diffusion denuders and a filter pack for collecting the various vapors released from a filter. A filter pack consists of two or more filters in series. A typical diffusion denuder is a chemically coated cylindrical tube that removes gases that diffuse to the walls and react with the coating. Particles are not removed because their diffusion coefficients are too low to cause significant diffusion to the tube walls. After sampling, the denuders can be extracted and analyzed for their ionic content. In past years, denuders were made with hollow tubes whose gas collection efficiencies are large only at very low flow rates. To obtain both high collection efficiency and high flow rate with hollow tube denuders, it is necessary to operate several denuder tubes in parallel (Stevens et al., 1978).

Possanzini et al. (1983) made a substantial improvement in denuder performance by using an annular denuder which collects gaseous pollutants by moving air through an annular space between two concentric glass cylinders coated with an appropriate chemical substrate. The cylinder walls are etched by sand blasting to increase their capacity to support the denuding chemical substrate. Collection E_h efficiency for a hollow tube denuder of length L is

$$E_h = 0.82 \exp [-3.66 (\pi DL/F)] \quad (12)$$

and efficiency E_a for an annular denuder of length L is

$$E_a = 0.82 \exp [-5.63 (\pi DL/F) (d_2 + d_1)/(d_2 - d_1)] \quad (13)$$

where D = species diffusion coefficient; d_2 = internal diameter of tube; d_1 = diameter of internal cylinder; F = flow rate (Possanzini et al., 1983). For a given tube length, an annular denuder can operate at 20 times the flow rate and yet have the same efficiency as a hollow tube. Moreover, laminar flow conditions

are maintained up to fairly high flow rate in an annular denuder (Possanzini et al., 1983).

Figure 3 and Table 10 represent an annular denuder system and filter pack that can measure a variety of gaseous and particulate species. The system has a cyclone on the inlet to remove coarse (>2.5 μm) particles. Three chemically treated denuders are used for selectively collecting the gases listed in Table 10. Denuders 1, 2 and 3 are quantitative for HNO_3, HNO_2 and NH_4, respectively, and the collection of SO_2 occurs on denuders 1 and 2. The filter pack consists of three filters in series. Vapors that volatilize from the first filter via reactions (6-11) are collected on filters 2 and 3 and enable the original ionic content of the sample to be deduced (Slater et al., 1989). Earlier systems did not use the first NaCl-coated denuder and attempted to distinguish HNO_2 from HNO_3 on the basis of the nitrite/nitrate ratio (Vossler et al., 1988; Koutrakis et al., 1988b), but this is unreliable because the collected nitrite can oxidize to nitrate during sampling.

Ionic species in denuder and filter extracts are determined by techniques described in sections 5.2 - 5.4. Analysis of SO_2 is simplified if any collected sulfite is oxidized to sulfate by adding 50 μL of 0.3% fresh H_2O_2 to each 2.5 mL of denuder extract before it is analyzed by ion chromatography.

The system described in Table 10 provides a reliable means to obtain concentrations of both gaseous and particulate species for use in receptor models. For example, such a system is useful for obtaining simultaneous SO_2 and $SO_4^=$ data in studies to determine the origins and age of sulfate aerosol. Also, such a system enables particulate and gas phase nitrate to be measured without bias due to nitrate evaporation in studies to determine contributions of particulate nitrate to visibility degradation.

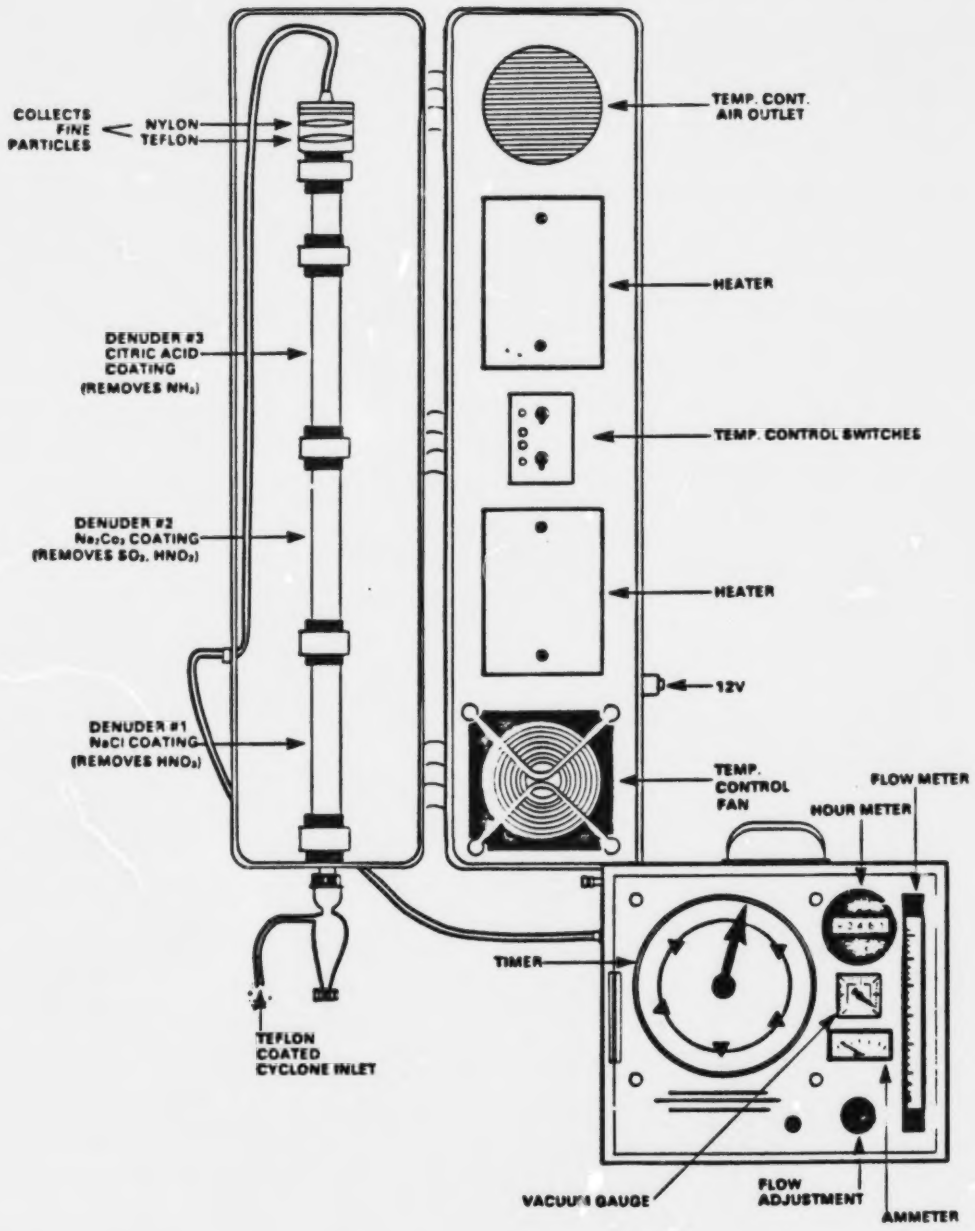

Figure 3. Schematic description of annular denuder system with filter pack.

Table 10. Annular denuder and filter pack system for collecting particulate and gaseous ionic species.

Stage	Substrate	Species collected	Species analyzed by ion chromatography
Denuder 1	NaCl + glycerine	HNO_3, SO_2	NO_3^-, $SO_4^=$
Denuder 2	$CaCO_3$ + glycerine	HNO_2, SO_2	NO_2^-, NO_3^-, $SO_4^=$
Denuder 3	Citric acid + glycerine	NH_3	NH_4^+
Filter 1	Ringed Teflon filter	particles	H^+, NH_4^+, NO_3^-, $SO_4^=$
Filter 2	Na_2CO_3 on glass filter	volatilized HNO_3	NO_3^-
Filter 3	Citric acid on glass	volatilized NH_3	NH_4^+

6 Conclusions

6.1 Analysis of quartz filters from PM-10 hi vol samplers

If the only available samples were collected on quartz filters, optical spectroscopy is the preferred method for determining element concentrations. The extraction and ICP methods developed by Harper et al. (1983) provide quantitative data for V, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ba and Pb. Such data can be used in receptor models to determine many sources, but additional data for Al and perhaps Ca and Sc are needed to determine soil. It is difficult to extract the Al from soil particles on a quartz filter, but Al can be measured on quartz by INAA with 5-min activation time. A portion of the quartz filter can be extracted in deionized water and analyzed by ion chromatography for sulfate and nitrate. Carbon can be determined by pyrolysis. Although sampling artifacts may cause the collected carbon and nitrate not to represent true atmospheric concentrations, the analyses will determine those components as they are represented in the measured PM-10 mass concentration.

6.2 Analysis of filters from dichotomous samplers

The use of dichotomous samplers may be preferred for collecting particles on Teflon filters since they can be analyzed inexpensively by XRF. Usually Al, Si, S, K, Ca, Ti, Mn, Fe, Zn, Br and Pb can be determined by EDXRF. Depending on the airshed and XRF procedure, Cl, V, Cr, Ni, Cu, Se, Sr, Cd, Sb and Ba can often be determined. Excellent precision for V can be obtained by EDXRF if precise data for Ba are available so that the Ba - V interference correction can be made algebraically. Such Ba data can be obtained by WDXRF. If better precision and additional elements are needed, WDXRF can be used to determine Al, Ti, Cd, Sn and Sb, and INAA can be used to determine Na, Al, Sc, V, Cr, Mn, Co, As, Se, Mo, Sb, La, Sm and Ce. Gordon et al. (1984) suggest that the cost of INAA can be reduced by using only a single 5-min irradiation, which can determine most of the elements in Groups 1, 2 and 3 in Table 7. Because this strategy does not determine Ce, which is emitted by refineries and automobile catalysts, selected samples could also be analyzed for elements in Group 4 by the more expensive 4-hour INAA irradiation (see Table 7).

It is not always necessary to measure sulfate because XRF data for S have been shown to be equivalent to ion chromatography data for sulfate in many airsheds (Stevens et al., 1978; Dzubay et al., 1988). Ion analysis is needed to determine nitrate, ammonium and hydrogen ion, but sampling artifacts can cause filter samples not to represent atmospheric concentrations of those ions. Use of an annular denuder system with a filter pack will enable those ions to be measured quantitatively, along with SO_2, HNO_3, and HNO_2 gases. If carbon data are needed, additional samples need to be collected on quartz filters. However, measurement uncertainty due to adsorption of organic vapors on quartz filters and ambiguity in measuring the C_e/C_v ratio discourages the use of carbon data in the chemical mass balance receptor model.

6.3 Quality assurance. To establish the precision and accuracy of the data, several of the following steps should be included in any measurement program: (1) Determine overall precision by analyzing samples collected in simultaneously operated duplicate samplers. (2) Determine XRF precision by reanalysis of 5 to 10% of the samples. Precision for ICP or INAA can be established by splitting samples and analyzing both portions. To avoid bias, the samples can be given new identification numbers known only to the one conducting the evaluation. (3) Determine the standard deviation for several blanks to provide an estimate of precision for elements with low concentration. Some of the blanks could be filters that were installed in a sampler that was not operated. (4) Analyze a subset of samples by two separate methods such as EDXRF and WDXRF or EDXRF and INAA to assess accuracy. (5) Determine accuracy by analyzing standard reference materials by a procedure identical to the one used for unknown samples.

6.4 Selection of analytical laboratories. When one lacks equipment or expertise to perform all needed analyses, assistance from another laboratory is required. Because receptor models require data with known precision and accuracy, the selected laboratory must be able to validate its results for air samples. Attention to the following criteria can be helpful in selecting a laboratory: (1) The laboratory has experience in successfully analyzing your kind of samples. (2) Measurement uncertainty is routinely reported with each reported datum. (3) Effects of interferences are included in all uncertainty estimates. (4) Measurement uncertainties have been previously validated by a quality assurance program like the one described in Section 6.3. (5) Adequate precision and accuracy have been demonstrated for your type of sample.

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